MULTI-COMPONENT COPOLYMER, PREPARATION METHOD THEREFOR, AND USE THEREOF, AND HALOGENATED BRANCHED BUTYL RUBBER, PREPARATION METHOD THEREFOR, AND USE THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The application claims the benefit of the China patent application No. "202211173637.1", filed on September 26, 2022, the content of which is specifically and entirely incorporated herein by reference.

FIELD

[0002] The present disclosure relates to the technical field of rubber preparation, in particular to a multi-component copolymer, a method therefor, and use thereof, and a halogenated branched butyl rubber, a method therefor, and use thereof.

BACKGROUND

[0003] Along with the rapid development of modern science and technology, the mechanical apparatuses in high-speed rail, aerospace, naval vessel, mechanical engineering, automobile, electronic appliances and other fields tend to be operated with the high-frequency and high-speed, which causes a series of problems such as high-frequency vibration and

noise although it brings convenience to the production and daily life. The problems not only accelerate fatigue damage of mechanical structural materials, shorten their service life, and bring forth the increasingly prominent threats to the safety of people's life and property. Therefore, vibration absorption and noise reduction have emerged as one of the problems urgently needed to be solved in the nowadays society. Therefore, the research and development of efficient damping materials with excellent performance and enhancing the use effects of damping and shock absorption is crucial for improving the operating environment of machines and ensuring the health and safety of human beings.

[0004] Diene rubber is an unsaturated rubber containing two C=C double bonds, and the industrial products are mainly cis-butyl rubber, iso-pentyl rubber, butyl rubber, etc. The diene rubber is widely used in various fields of production and daily life. However, butyl rubber has a higher unsaturation degree in the molecular chain and the substituent methyl groups are symmetrically arranged, such a molecular structure determines its inevitable defects such as poor ozone aging resistance, long vulcanization and scorching time, low vulcanization rate, and poor damping performance, it results in that the butyl rubber cannot meet the increasingly diverse processing requirements and use scenarios, the defects have become a bottleneck for expanding use of butyl rubber material.

[0005] Brominated Isobutylene Isoprene Rubber (BIIR) is obtained by

introducing bromine atoms into the molecular chain of Isobutylene Isoprene Rubber (IIR) and performing an electrophilic substitution reaction under the effect of molecular bromine. BIIR has the same excellent air-tightness as IIR, the BIIR further exhibits advantages such as excellent adhesiveness, high vulcanization rate, good thermal stability and corrosion resistance, it can be used in extreme environments such as highly corrosive or high temperature environments. Secondly, due to the introduction of bromine atoms, the molecular chain polarity of the BIIR is increased, the relaxation resistance of the chain segment is incremented, and the internal friction is high, thus the BIIR has excellent damping performance, it is one of the most widely used basic damping rubbers.

[0006] In the practical use at present, it is often required that the damping materials perform the damping function within the temperature range from -50°C to +50°C, however, the BIIR has a defect that its effective damping functional region (damping factor $\tan\delta > 0.3$) is mainly concentrated on the low temperature segment, the damping value is low at the temperature above 15°C, thus BIIR cannot desirably meet the application requirements for the wide temperature-region damping materials, therefore, how to broaden the effective damping functional region of the butyl-based rubber at the temperature above room temperature is one of the research hotspots of rubber damping materials today.

[0007] CN112574333A discloses a bromination process of star-branched

butyl rubber, the bromination process comprises the following steps: a) dissolving the star-branched butyl rubber in aliphatic hydrocarbon to obtain a rubber solution; b) mixing the glue solution with a branching agent capturing agent ethanol to obtain a mixed solution; c) adding an oxidizing agent hydrogen peroxide and a brominating agent Br_2 to the mixed solution, and arranging a molar ratio of bromine element to unsaturated double bond in the star-branched butyl rubber to be (0.75-2): 1, performing bromination reaction, final neutralization, and product recovery to obtain the brominated star-branched butyl rubber.

[0008] CN106749816A discloses a preparation method of brominated butyl rubber. The method comprises the following steps: initially dissolving butyl rubber with n-alkane, then performing the bromination reaction in a solvent by using a specific organic bromide (e.g., phenyltrimethylamine tribromide, benzyl trimethyl ammonium tribromide, dibromoisocyanuric acid) as a brominating agent, and using Br_2 or HBr as a bromination accelerator to obtain the brominated butyl rubber.

[0009] Mingyi Liao et al . (*Journal of Dalian Maritime University*, 2008, 34(2):83-86) disclosed a method to improve the damping performance of butyl rubber (IIR) by using a stepwise approach, in which isobutylene-isoprene rubber (IIR) as polymer network I, poly(styrene-methyl methacrylate) [P(St-MMA)] as polymer network II, and through the grafting polymerization, a butyl rubber/poly (styrene-methyl methacrylate)

interpenetrating polymer network [IIR/P(St-MMA)IPN] was successfully prepared, the isobutylene-isoprene rubber material with a wide temperature range and high damping performance was prepared.

[0010] Although the prior art can widen the effective damping temperature range of rubber and improve the damping performance of rubber to some extent through the blending method, copolymerization method, and interpenetrating network polymer method, and the like, there are still some limitations of these methods, which may result in problems such as deterioration of mechanical properties of rubber material, complicated process, difficulties in practical operation, large addition amount, high cost, environmental pollution resulting from the difficulty in removing organic solvents.

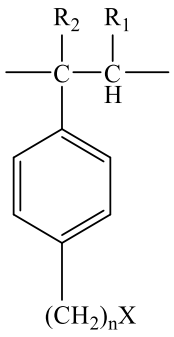
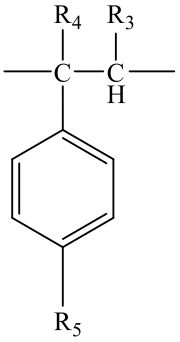
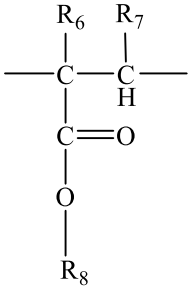
[0011] Therefore, it is urgently needed to develop a rubber material having a wide effective damping temperature range, high damping performance, excellent mechanical properties, and the pollution-free preparation method that can be easily operated.

SUMMARY

[0012] The present disclosure aims to overcome the defects in the prior art with respect to that the rubber materials cannot balance a wide effective damping temperature range, high damping performance, desirable mechanical properties, and the pollution caused by the complicated

preparation process, and provide a multi-component copolymer, a method therefor, and use thereof, and a halogenated branched butyl rubber, a method therefor, and use thereof.

[0013] In order to achieve the above objects, the first aspect of the present disclosure provides a multi-component copolymer comprising a structural unit A, a structural unit B, and a structural unit C, wherein the structural unit A has a structure represented by formula (1), the structural unit B has a structure represented by formula (2), and the structural unit C has a structure represented by formula (3);

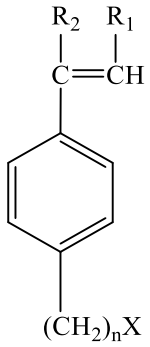
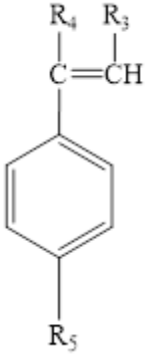
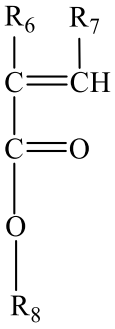
[0014]  Formula (1)  Formula (2)  Formula (3)

[0015] wherein R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 are each independently hydrogen or a C_1-C_{10} linear chain or branched alkyl; X is halogen, and n is any integer of 1 to 10;

[0016] the tail end of the multi-component copolymer contains a structural unit from a conjugated diene.

[0017] The second aspect of the present disclosure provides a method for preparing a multi-component copolymer comprising: subjecting a monomer represented by formula (I), a monomer represented by formula

(II), and a monomer represented by formula (III) to a polymerization reaction under a polymerization reaction conditions and in the presence of an initiator, an optional structural modifier, and an organic solvent to obtain a polymer solution;

[0018]  Formula (I)  Formula (II)  Formula (III)

[0019] adding a conjugated diene monomer into the polymer solution to carry out an end-capping reaction to prepare the multi-component copolymer;

[0020] wherein R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 are each independently hydrogen or a C_1-C_{10} linear chain or branched alkyl; X is halogen, and n is any integer of 1 to 10.

[0021] The third aspect of the present disclosure provides a multi-component copolymer produced with the aforementioned method.

[0022] The fourth aspect of the present disclosure provides a use of the aforementioned multi-component copolymer as a grating agent in the preparation of the diene rubber.

[0023] The fifth aspect of the present disclosure provides a halogenated

branched butyl rubber comprising a structural unit I from isobutylene, a structural unit II from isoprene, and a structural unit III from halogenated grafting agent; wherein the halogenated grafting agent is the aforementioned multi-component copolymer.

[0024] The sixth aspect of the present disclosure provides a method for preparing the aforementioned halogenated branched butyl rubber comprising: contacting isobutylene and isoprene with the aforementioned multi-component copolymer in the presence of a diluent, an organic solvent, and a co-initiator for performing the cationic polymerization to prepare the halogenated branched butyl rubber.

[0025] The seventh aspect of the present disclosure provides a halogenated branched butyl rubber produced with the aforementioned preparation method.

[0026] The eighth aspect of the present disclosure provides a use of the aforementioned halogenated branched butyl rubber in instrument shock absorbers and electric appliance vibration absorbers.

[0027] Due to the above technical scheme, the present disclosure produces the favorable technical effects as follows:

[0028] (1) The multi-component copolymer provided by the present disclosure combines p-alkyl phenyl, p-halogenated alkylbenzene, and ester groups on a macromolecular chain to form an Interpenetrating Polymer Network (IPN), such that the p-alkyl phenyl, the halogen atoms, and the

ester groups have the characteristics such as high rigidity, large steric hindrance, and strong adsorptive power; when the multi-component copolymer is used as a halogenated grafting agent for preparing a halogenated branched butyl rubber, it can generate a remarkable "synergistic effect " in broadening the effective damping temperature range of the halogenated branched butyl rubber, greatly broaden the effective damping temperature range of the halogenated branched butyl rubber, the prepared halogenated branched butyl rubber has a wide temperature range, high damping property, an effective damping temperature range ($\tan\delta \geq 0.3$) exceeding the range from -50°C to 62°C, and the maximum damping factor $\tan\delta_{max}$ larger than 1.9.

[0029] (2) The p-alkyl phenyl, p-halogenated alkylbenzene, and ester groups in the multi-component copolymer of the present disclosure are arranged on a macromolecular chain, resulting in the superposition of "group effect" and "structure effect". When the multi-component copolymer is used as a halogenated grafting agent for preparing a halogenated branched butyl rubber, it not only avoids the degraded damping property of the halogenated branched butyl rubber due to broadening of the effective damping temperature range, but also avoids the problem that the branching causes broadening of the molecular weight distribution, resulting in the degraded mechanical property and gas tightness of the butyl rubber, thereby improving the tensile strength and

gas tightness of the butyl rubber.

[0030] (3) The halogenated branched butyl rubber prepared in the present disclosure is produced by using a multi-component copolymer as the grafting agent through an addition polymerization instead of an ion substitution, it obstructs the conditions of halogen structure isomerization, improves stability of effective damping temperature range and damping performance of the halogenated branched butyl rubber, broadens the application scope of the halogenated branched butyl rubber.

[0031] (4) The present disclosure has no emission of Volatile Organic Compound (VOC) and the byproduct HBr during the preparation process of halogenated branched butyl rubber, the method has the characteristics such as environmental protection, a short technological process, a low production cost, and suitability for the industrial production.

BRIEF DESCRIPTION OF THE DRAWINGS

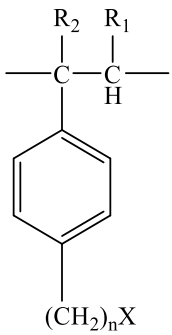
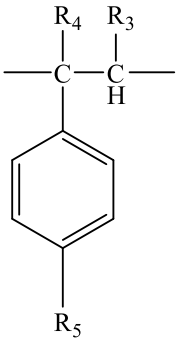
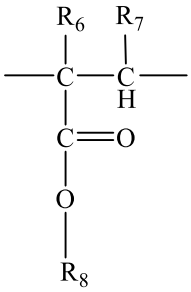
[0032] FIG. 1 illustrates a dynamic mechanical spectrogram of a brominated branched butyl rubber product (Curve #1) prepared in Example 11 of the disclose and an existing Brominated Isobutylene Isoprene Rubber (BIIR) 2302 (Curve #2).

DETAILED DESCRIPTION

[0033] The terminals and any value of the ranges disclosed herein are not

limited to the precise ranges or values, such ranges or values shall be comprehended as comprising the values adjacent to the ranges or values. As for numerical ranges, the endpoint values of the various ranges, the endpoint values and the individual point values of the various ranges, and the individual point values may be combined with one another to produce one or more new numerical ranges, which should be deemed to have been specifically disclosed herein.

[0034] The first aspect of the present disclosure provides a multi-component copolymer comprising a structural unit A, a structural unit B, and a structural unit C, wherein the structural unit A has a structure represented by formula (1), the structural unit B has a structure represented by formula (2), and the structural unit C has a structure represented by formula (3);

[0035]  Formula (1)  Formula (2)  Formula (3)

[0036] wherein R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 are each independently hydrogen or a C_1-C_{10} linear chain or branched alkyl; X is halogen, and n is any integer of 1 to 10;

[0037] the tail end of the multi-component copolymer contains a structural

unit from a conjugated diene.

[0038] The multi-component copolymer of the present disclosure comprises p-alkyl phenyl, p-halogenated alkylbenzene, and ester groups to form an Interpenetrating Polymer Network (IPN), so that the p-alkyl phenyl, the halogen atoms, and ester groups have the characteristics such as high rigidity, large steric hindrance, and strong adsorptive power, and the tail end of the copolymer contains a conjugated diene structural unit, thus the multi-component copolymer exhibits a high polymerization activity, can be used as a grafting agent for the preparation of a branched diene rubber, in particular, for the preparation of a halogenated branched diene rubber.

[0039] In the present disclosure, the examples of said C_1-C_{10} linear chain or branched alkyl may be any one of methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, t-butyl, n-pentyl, isopentyl, t-pentyl, neo-pentyl, n-hexyl, isohexyl, n-heptyl, isoheptyl, 2-methylhexyl, 2-ethylhexyl, 1-methylheptyl, 2-methylheptyl, n-octyl, iso-octyl, n-nonyl, isononyl, and 3,5, 5-trimethylhexyl.

[0040] In the present disclosure, the value of n in the structure represented by formula (1) may be selected from 1, 2, 3, 4, 5, 6, 7, 8, 9, 10.

[0041] In some embodiments of the present disclosure, wherein R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 are each independently hydrogen or a C_1-C_6 linear chain or branched alkyl, preferably hydrogen or a C_1-C_4 linear chain or

branched alkyl, more preferably hydrogen, methyl, or ethyl.

[0042] In some preferred embodiments of the present disclosure, R_6 is methyl.

[0043] In some preferred embodiments of the present disclosure, X is selected from Cl and/or Br.

[0044] In some preferred embodiments of the present disclosure, n is any integer of 1 to 5, preferably any integer of 1 to 3.

[0045] In some preferred embodiments of the present disclosure, the conjugated diene is butadiene and/or isoprene.

[0046] In some preferred embodiments of the present disclosure, the structural unit represented by formula (1) may be a structural unit from p-bromomethyl styrene, the structural unit represented by formula (2) may be a structural unit from p-alkyl styrene, such as p-methyl styrene, p-ethyl styrene, p-propyl styrene, p-n-butyl styrene, p-isobutyl styrene, or p-isoamyl styrene, and the structural unit represented by formula (3) may be a structural unit from an unsaturated acrylate, such as a structural unit derived from methyl methacrylate (MMA), ethyl methacrylate, butyl methacrylate, or tert-butyl methacrylate.

[0047] In the present disclosure, the multi-component copolymer is a block copolymer or a random copolymer.

[0048] In some embodiments of the present disclosure, the mass ratio of structural unit A, structural unit B, structural unit C, and the structural unit

from a conjugated diene is 100: (20-50): (10-25): (1-5), such as 100:20:25:1, 100:50:10:5, 100:30:15:2, 100:40:20:4, 100:25:12:3, and a random value within the range consisting of any two numerical values, preferably is 100: (30-40): (15-20): (2-3). When the mass ratio of structural units in the multi-component copolymer falls into the above ranges, the prepared halogenated branched butyl rubber has a wide temperature range, a high damping property, an effective damping temperature range ($\tan\delta \geq 0.3$) exceeding the range from -50°C to 62°C, the maximum damping factor $\tan\delta_{max}$ larger than or equal to 1.9, and a tensile strength within the range of 22MPa-24MPa.

[0049] The above ratios may be measured by means of infrared spectroscopy and nuclear magnetic resonance, or be determined according to the relationship of feedstock during the preparation process.

[0050] In some preferred embodiments of the present disclosure, the mas percentage content of the halogen in the multi-component copolymer is within the range of 2.5-5.5%, such as 2.5%, 3%, 3.5%, 4%, 4.5%, 5%, 5.5%, and a random value within the range consisting of any two numerical values, preferably within the range of 4-5%. When the mass percentage content of the halogen in the multi-component copolymer meets the above ranges, the damping performance and vulcanization processability of butyl rubber can be improved. In the present disclosure, the halogen content is measured by using the Q600 type TG/DTG thermogravimetric analyzer.

[0051] In some embodiments of the present disclosure, the multi-component copolymer has a number average molecular weight (Mn) within the range of 25,000-60,000 g/mol, such as 25,000 g/mol, 30,000 g/mol, 35,000 g/mol, 400,000 g/mol, 45,000 g/mol, 50,000 g/mol, 60,000 g/mol, and a random value within the range consisting of any two numerical values, preferably within the range of 40,000-50,000 g/mol.

[0052] In some preferred embodiments of the present disclosure, the multi-component copolymer has a molecular weight distribution index (Mw/Mn) within the range of 1.2-2, such as 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2, and a random value within the range consisting of any two numerical values, preferably within the range of 1.45-1.95.

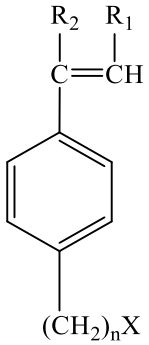
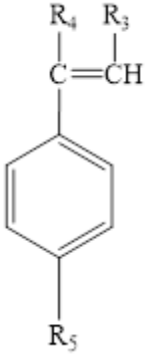
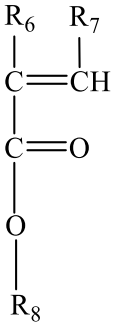
[0053] In the present disclosure, both the number average molecular weight and the molecular weight distribution index are measured by gel chromatography.

[0054] In some embodiments of the present disclosure, the multi-component copolymer has an apparent viscosity within the range of 8-40cps at 25°C.

[0055] In the present disclosure, the apparent viscosity of a multi-component copolymer at 25°C is tested using the Ubbelohde viscometer according to the China National Standard GB/T 10247-2008.

[0056] The second aspect of the present disclosure provides a method for preparing a multi-component copolymer comprising the following steps:

subjecting a monomer represented by formula (I), a monomer represented by formula (II), and a monomer represented by formula (III) to a polymerization reaction under a polymerization reaction conditions and in the presence of an initiator, an optional structural modifier, and an organic solvent to obtain a polymer solution;

[0057]  Formula (I)  Formula (II)  Formula (III)

[0058] adding a conjugated diene monomer into the polymer solution to carry out an end-capping reaction to prepare a multi-component copolymer;

[0059] wherein R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 are each independently hydrogen or a C_1-C_{10} linear chain or branched alkyl; X is halogen, and n is any integer of 1 to 10.

[0060] The method in the present disclosure has the characteristics that the reaction is complete, the byproduct is not generated, the produced multi-component copolymer exhibits a stable structure and a regularly arranged molecular chain.

[0061] In some embodiments of the present disclosure, wherein R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 are each independently hydrogen or a C_1-C_6 linear

chain or branched alkyl, preferably hydrogen or a C_1-C_4 linear chain or branched alkyl, more preferably hydrogen, methyl, or ethyl.

[0062] In some preferred embodiments of the present disclosure, R_6 is methyl.

[0063] In some preferred embodiments of the present disclosure, X is selected from Cl and/or Br.

[0064] In some preferred embodiments of the present disclosure, n is any integer from 1 to 5, preferably from 1 to 3.

[0065] Examples of C_1-C_{10} linear chain or branched alkyl according to the second aspect of the present disclosure are as described above for those of the first aspect of the present disclosure, the content will not be repeatedly described herein.

[0066] In some embodiments, the monomer represented by formula (I) is p-bromomethyl styrene, the monomer represented by formula (II) is p-methyl styrene, p-ethyl styrene, p-propyl styrene, p-n-butyl styrene, p-isobutyl styrene, or p-isoamyl styrene, and the monomer represented by formula (III) is methyl methacrylate (MMA), ethyl methacrylate, butyl methacrylate, or tert-butyl methacrylate.

[0067] In some embodiments of the present disclosure, wherein the conjugated diene is butadiene and/or isoprene.

[0068] In some preferred embodiments of the present disclosure, the mass ratio of the monomer represented by formula (I), the monomer represented

by formula (II), the monomer represented by formula (III), and the conjugated diene is 100: (20-50) : (10-25) : (1-5), such as 100:20:25:1, 100:50:10:5, 100:30:15:2, 100:40:20:4, 100:25:12:3, and a random value within the range consisting of any two numerical values, preferably 100: (30-40) : (15-20): (2-3). In the present disclosure, when the mass ratio of the monomer represented by formula (I), the monomer represented by formula (II), the monomer represented by formula (III), and the conjugated diene is controlled to be within the specific ranges, the prepared butyl rubber has an effective damping temperature range ($\tan\delta \geq 0.3$) exceeding the range from -50°C to 62°C, and the maximum damping factor $\tan\delta_{max}$ larger than or equal to1.9.

[0069] In some preferred embodiments of the present disclosure, the polymerization reaction is carried out under a protective atmosphere, preferably an inert atmosphere.

[0070] In some preferred embodiments of the present disclosure, the initiator is a hydrocarbon-based monolithium compound, preferably RLi, wherein R is at least one selected from the group consisting of C_1-C_{20} saturated aliphatic hydrocarbon group, C_3-C_{20} alicyclic hydrocarbon group, and C_6-C_{20} aromatic hydrocarbon group.

[0071] In some preferred embodiments of the present disclosure, the initiator is at least one selected from the group consisting of n-butyl lithium, sec-butyl lithium, methyl butyl lithium, phenyl butyl lithium, naphthyl

lithium, cyclohexyl lithium, and dodecyl lithium. In the present disclosure, by selecting the above initiator, the monomers can carry out the anionic polymerization to form a block copolymer, thereby achieving the superposition of "group effect" and "structure effect".

[0072] In some preferred embodiments of the present disclosure, the initiator is used in an amount of 16-30mmo1, preferably 18-25 mmol, relative to 1,000g of the monomer represented by formula (I). if the initiator dosage is insufficient, the prepared multi-component copolymer has a small molecular weight, which may affect the broad temperature range and damping performance of the butyl rubber in use, the desired modification effect cannot be achieved; if the initiator dosage is excessive, the prepared multi-component copolymer has a widened molecular weight distribution, the butyl rubber exhibits the degraded gas tightness and mechanical strength.

[0073] In some preferred embodiments of the present disclosure, the structural modifier is a polar organic compound.

[0074] The structural modifier of the present disclosure is a polar organic compound, which is capable of producing a solvation effect in a polymerization system, and adjusting the reactivity ratio of an alkyl styrene and isoprene so that the two compounds carry out the block copolymerization.

[0075] In some preferred embodiments of the present disclosure, the

structural modifier is at least one selected from the group consisting of diethylene glycol dimethyl ether, tetrahydrofuran, diethyl ether, ethyl methyl ether, anisole, diphenyl ether, ethylene glycol dimethyl ether, and triethylamine.

[0076] In some preferred embodiments of the present disclosure, the organic solvent is a hydrocarbon solvent, preferably at least one selected from the group consisting of straight-chain alkane, aromatic hydrocarbon, and cyclane, further preferably at least one selected from the group consisting of pentane, hexane, octane, heptane, cyclohexane, benzene, toluene, xylene, and ethylbenzene.

[0077] In some embodiments, the polymerization reaction conditions comprise a polymerization reaction temperature within the range of 50-80°C, such as 50°C, 60°C, 70°C, 80°C, and a random value within the range consisting of any two numerical values. If the polymerization reaction temperature is too low, it results in the reduced reactivity, decreased reaction rate, incomplete reaction process, the desired modification effects of broad temperature range and high damping performance of the butyl rubber cannot be obtained in use; if the polymerization reaction temperature is too high, it causes the increased reactivity, larger reaction rate, irregular arrangement of molecular structure, and reduced strength and gas tightness of the butyl rubber in use.

[0078] The polymerization reaction time is within the range of 220-

270min, for example, 220 min, 230 min, 240 min, 250 min, 260 min, 270min, and a random value within the range consisting of any two numerical values. If the polymerization reaction time is too short, the desired modification effects of broad temperature range and high damping performance of the butyl rubber cannot be obtained in use; if polymerization reaction time is too long, it results in the high energy consumption, and the obvious modification effects of broad temperature range and high damping performance of the butyl rubber cannot be achieved in use.

[0079] In some preferred embodiments of the present disclosure, the end-capping reaction temperature is within the range of 60-90°C, such as 60°C, 65°C, 70°C, 75°C, 80°C, 85°C, 90°C, and a random value within the range consisting of any two numerical values, preferably within the range of 70-80°C. If the end-capping reaction temperature is too low, it results in the incomplete end-capping process, reduced reaction active sites, decreased grafting rate, the modification effects of broad temperature range and high damping performance of the butyl rubber are poor in use; if the end-capping reaction temperature is too high, the conjugated diene is prone to perform auto-polymerization and unable to perform the end-capping action. The end-capping reaction time is within the range of 10-45 min, such as 10 min, 15 min, 20 min, 25 min, 30 min, 35 min, 40 min, 45min, preferably within the range of 20-30 min. If the end-capping reaction time is too short,

it results in the incomplete end-capping process, reduced reaction active sites, the modification effects of broad temperature range and high damping performance of the butyl rubber cannot be produced in use; if the end-capping reaction time is too long, it results in the increased flexibility of the chain segment of the prepared multi-component copolymer, and the damping performance and mechanical strength of butyl rubber will be damaged in use.

[0080] In some embodiments of the present disclosure, the method comprises the following steps:

[0081] (1) mixing a monomer represented by formula (I), a structural modifier, a solvent, and an initiator to perform a first polymerization reaction to obtain a first polymerization product;

[0082] (2) adding a monomer represented by formula (II) and a structural modifier into the first polymerization product, then mixing the materials to perform a second polymerization reaction to obtain a second polymerization product;

[0083] (3) adding a monomer represented by formula (III) and a structural modifier into the second polymerization product, then mixing the materials to perform a third polymerization reaction to obtain a third polymerization product;

[0084] (4) adding a conjugated diene into the third polymerization product for performing an end-capping reaction to prepare the multi-component

copolymer.

[0085] In the preparation method of the present disclosure, a multi-component copolymer having tri-block can be produced by using an anionic polymerization method, the multi-component copolymer has the characteristics such as a controlled structure, a stable bromine structure, a high isotacticity, a complete reaction, no byproduct, and it can bring about the effects that the halogenated branched diene rubber exhibits a wide applicable temperature range, a high damping property, and excellent mechanical strength and vulcanization processability.

[0086] In some preferred embodiments of the present disclosure, the mass ratio of the monomer represented by formula (I) to the structural modifier in step (1) is 100: (0.5-0.7), such as 100:0.5, 100:0.6, 100:0.7, and a random value within the range consisting of any two numerical values. By controlling the mass ratio of the monomer represented by formula (I) to the structural modifier in step (1) within the aforementioned ranges, the block polymer with a high isotacticity can be produced.

[0087] In some preferred embodiments of the present disclosure, the mass ratio of the monomer represented by formula (II) to the structural modifier in step (2) is (30-40) : (0.3-0.5), such as 30:0.3, 35:0.35, 40:0.5, and a random value within the range consisting of any two numerical values. By controlling the mass ratio of the monomer represented by formula (II) to the structural modifier in step (2) within the aforementioned ranges, the

block polymer with a high isotacticity can be produced.

[0088] In some preferred embodiments of the present disclosure, the mass ratio of the monomer represented by formula (III) to the structural modifier in step (3) is (15-20) : (0.2-0.3), such as 15:0.2, 18:0.25, 20:0.3, and a random value within the range consisting of any two numerical values. By controlling the mass ratio of the monomer represented by formula (III) to the structural modifier in step (3) within the aforementioned ranges, the block polymer with a high isotacticity can be produced.

[0089] In some embodiments of the present disclosure, the first polymerization reaction temperature is within the range of 40-80°C, such as 40°C, 45°C, 55°C, 65°C, 70°C, 75°C, 80°C, and a random value within the range consisting of any two numerical values, preferably within the range of 50-60°C. If the first polymerization reaction temperature is too low, it will result in an excessively low bromine content; if the first polymerization reaction temperature is too high, it may destroy the bromine structure. The first polymerization reaction time is within the range of 80-150 min, such as 80 min, 90 min, 100 min, 110 min, 120min, 130 min, 140 min, 150min, and a random value within the range consisting of any two numerical values, preferably within the range of 100-120min. If the first polymerization reaction time is too short, it results in a lower molecular weight and a decreased bromine content; if the first polymerization reaction time is too long, the molecular weight change is

not obvious, and the modification effect is not remarkable.

[0090] In some preferred embodiments of the present disclosure, the second polymerization reaction temperature is within the range of 60-90°C, such as 60°C, 65°C, 70°C, 75°C, 80°C, 85°C, 90°C, and a random value within the range consisting of any two numerical values, preferably within the range of 70-80°C. If the second polymerization reaction temperature is too low, it will cause an excessively low content of benzene ring structure, resulting in decreased strength and gas tightness; if the second polymerization reaction temperature is too high, the damping modification effect is not obvious. The second polymerization reaction time is within the range of 50-80 min, for example, 50 min, 55 min, 60min, 65 min, 70 min, 75 min, 80 min, and a random value within the range consisting of any two numerical values, preferably within the range of 60-70 min. If the second polymerization reaction time is too short, it will result in a smaller molecular weight, a decreased benzene ring structure, and a small increase amplitude of damping performance; if the second polymerization reaction time is too long, it causes a high energy consumption, no significant change in benzene ring structure, and no obvious change in the increase amplitude of damping performance.

[0091] In some preferred embodiments of the present disclosure, the third polymerization reaction temperature is within the range of 60-90°C, such as 60°C, 65°C, 70°C, 75°C, 80°C, 85°C, 90°C, and a random value within

the range consisting of any two numerical values, preferably within the range of 70-80°C. If the third polymerization reaction temperature is too low, it will cause that the polar ester group content is excessively low, resulting in narrowed damping temperature range of butyl rubber in use; if the third polymerization reaction temperature is too high, it causes an unapparent broadening of the applicable temperature range of butyl rubber in use. The third polymerization reaction time is within the range of 30-60 min, such as 30 min, 35 min, 40 min, 45 min, 50 min, 55 min, 60min, and a random value within the range consisting of any two numerical values, preferably within the range of 40-50 min. If the third polymerization reaction time is too short, it will cause that the polar ester group content is excessively low, the modification effect of broad temperature range of butyl rubber in use cannot be achieved; if the third polymerization reaction time is too long, it causes an unapparent broadening amplitude of the applicable temperature range of butyl rubber in use.

[0092] According to a particularly preferred embodiment of the present disclosure, the multi-component copolymer is prepared by adding an organic solvent, p-bromomethyl styrene and a structural modifier sequentially in sequence into a polymerizing pot under an inert atmosphere, heating to a temperature of 50-60°C and then adding an initiator for carrying out the reaction for 100-120 minutes, subsequently adding p-alkyl styrene and a structural modifier into the polymerizing pot, and further

heating to a temperature of 70-80°C and performing the reaction for 60-70 minutes, then adding an unsaturated acrylate and a structural modifier into the polymerizing pot and carrying out the reaction for 40-50 minutes, and finally adding isoprene into the polymerizing pot for performing an end-capping reaction for 20-30 minutes until no free monomer is present, the glue solution is subjected to a wet-condensing process and drying.

[0093] wherein the mass ratio of p-bromomethyl styrene, p-alkyl styrene, unsaturated acrylate, and isoprene is 100 : (30-40) : (15-20) : (2-3);

[0094] The mass ratio of the p-bromomethyl styrene and the structural modifier is 100 : (0.5-0.7);

[0095] The mass ratio of the p-alkyl styrene and the structural modifier is (30-40) : (0.3-0.5);

[0096] The mass ratio of the unsaturated acrylate to the structural modifier is (15-20) : (0.2-0.3).

[0097] The third aspect of the present disclosure provides a multi-component copolymer produced with the aforementioned preparation method.

[0098] The fourth aspect of the present disclosure provides a use of the aforementioned multi-component copolymer as a grating agent in the preparation of the diene rubber.

[0099] In some embodiments of the present disclosure, the diene rubber is butyl rubber.

[00100] The fifth aspect of the present disclosure provides a halogenated branched butyl rubber comprising: a structural unit I from isobutylene, a structural unit II from isoprene, and a structural unit III from halogenated grafting agent;

[00101] wherein the halogenated grafting agent is the aforementioned multi-component copolymer.

[00102] In some embodiments of the present disclosure, the mass ratio of said structural unit I, said structural unit II, and said structural unit III is 100: (4-6) : (7-10), such as 100:4:7, 100:5:6, 100:6:10, and a random value within the range consisting of any two numerical values, based on the total weight of the halogenated branched butyl rubber. In the present disclosure, when the mass ratio of said structural unit I, said structural unit II, and said structural unit III is controlled within a specific range, the prepared butyl rubber has an effective damping temperature range ($\tan\delta \geq 0.3$) exceeding the range from -50°C to 62°C, the maximum damping factor $\tan\delta_{max}$ larger than or equal to 1.9, and a tensile strength within the range of 22MPa-24MPa.

[00103] The multi-component copolymer provided by the present disclosure combines p-alkyl phenyl, p-halogenated alkylbenzene, and ester groups on a macromolecular chain to form an Interpenetrating Polymer Network (IPN), such that the p-alkyl phenyl, the halogen atoms and the ester groups have the characteristics such as high rigidity, large steric

hindrance, and strong adsorptive power; when the multi-component copolymer is used as a halogenated grafting agent for preparing a halogenated branched butyl rubber, it can generate a remarkable "synergistic effect " in broadening the effective damping temperature range of the halogenated branched butyl rubber, greatly broaden the effective damping temperature range of the halogenated branched butyl rubber, the prepared halogenated branched butyl rubber has a wide temperature range, high damping property, an effective damping temperature range ($\tan\delta \geq 0.3$) exceeding the range from -50°C to 62°C, and the maximum damping factor $\tan\delta_{max}$ larger than 1.9.

[00104] The sixth aspect of the present disclosure provides a method for preparing the aforementioned halogenated branched butyl rubber comprising:

[00105] contacting isobutylene and isoprene with the aforementioned multi-component copolymer in the presence of a diluent, an organic solvent, and a co-initiator for performing the cationic polymerization to prepared the halogenated branched butyl rubber.

[00106] The halogenated branched butyl rubber prepared in the present disclosure is produced by using a multi-component copolymer as the grafting agent through an addition polymerization instead of an ion substitution, it obstructs the conditions of halogen structure isomerization, improves stability of effective damping temperature range and damping

performance of the halogenated branched butyl rubber, broadens the application scope of the halogenated branched butyl rubber. The halogenated branched butyl rubber prepared in the present disclosure has an effective damping temperature range (tanδ ≥0.3) exceeding the range from -50°C to 62°C.

[00107] In addition, the present disclosure has no emission of Volatile Organic Compound (VOC) and the byproduct HBr during the preparation process, the method has the characteristics such as environmental protection, a short technological process, a low production cost, and suitability for the industrial production.

[00108] In some embodiments of the present disclosure, the mass ratio of isobutylene, isoprene and the aforementioned multi-component copolymer is 100: (4-6) : (7-10), such as 100:4:7, 100:5:6, 100:6:10, and a random value within the range consisting of any two numerical values. In the present disclosure, the mass ratio of isobutylene, isoprene, and the aforementioned multi-component copolymer is controlled within the specific range, the complete reaction of the multi-component copolymer in the preparation reaction of butyl rubber can be effectively ensured.

[00109] In some preferred embodiments of the present disclosure, the diluent is a halogenated alkane, wherein the halogen atom in the halogenated alkane is preferably F, Cl, or Br, and the number of carbon atoms in the halogenated alkane is preferably from 1 to 4, such as 1, 2, 3,

4.

[00110] In some preferred embodiments of the present disclosure, the diluent is at least one selected from the group consisting of methane chloride, methylene chloride, carbon tetrachloride, dichloroethane, tetrachloropropane, heptachloropropane, fluoromethane, difluoromethane, tetrafluoroethane, carbon hexafluoride, and fluorobutane.

[00111] In some preferred embodiments of the present disclosure, the mass ratio of said isobutene to said diluent is 100: (180-320), such as 100:180, 100:220, 100:250, 100:300, 100:320, and a random value within the range consisting of any two numerical values. In the present disclosure, a butyl rubber having a high molecular weight can be produced by controlling the mass ratio of isobutylene to the diluent within the specific range.

[00112] In some preferred embodiments of the present disclosure, the organic solvent is a hydrocarbon solvent, preferably at least one of straight-chain alkane, aromatic hydrocarbon, and cyclane, and further preferably at least one selected from the group consisting of pentane, hexane, octane, heptane, cyclohexane, benzene, toluene, xylene, and ethylbenzene.

[00113] The dosage of the organic solvent is not particularly limited in the present disclosure, the organic solvent may be added according to the conventional dosage in the art.

[00114] In some preferred embodiments of the present disclosure, the

co-initiator comprises an alkyl aluminum halide and a protic acid.

[00115] In some preferred embodiments of the present disclosure, the molar ratio of said alkyl aluminum halide to said protic acid in the co-initiator is (10-100) : 1, such as 10:1, 20:1, 30:1, 40:1, 50:1, 60:1, 70:1, 80:1, 90:1, 100:1, and a random value within the range consisting of any two numerical values.

[00116] In some preferred embodiments of the present disclosure, the alkyl aluminum halide is at least one selected from the group consisting of diethyl aluminum monochloride, diisobutyl aluminum monochloride, methyl aluminum dichloride, ethyl aluminum sesquichloride, isobutyl aluminum sesquichloride, n-propyl aluminum dichloride, isopropyl aluminum dichloride, dimethyl aluminum chloride, and ethyl aluminum chloride.

[00117] In some preferred embodiments of the present disclosure, the protonic acid is at least one selected from the group consisting of HCl, HF, HBr, H_2SO_4, H_2CO_3, H_3PO_4 and HNO_3.

[00118] In some preferred embodiments of the present disclosure, the mass ratio of said isobutene to said co-initiator is 100 : (0.1-0.3), such as 100:0.1, 100:0.15, 100:0.2, 100:0.25, 100:0.3, and a random value within the range consisting of any two numerical values.

[00119] In some preferred embodiments of the present disclosure, the cationic polymerization conditions comprise: the cationic polymerization

temperature from -100°C to -75°C, such as -100°C, -95°C, -90°C, -85°C, -80°C, -75°C, and a random value within the range consisting of any two numerical values. If the cationic polymerization temperature is too low, it causes that the reaction time is excessively long, and the structure cannot be easily controlled; if the cationic polymerization temperature is too high, it is prone to cause the chain transfer reaction, resulting in a decreased molecular weight. The cationic polymerization time is within the range of 3-4 hours, such as 3 hours, 3.2 hours, 3.4 hours, 3.6 hours, 3.8 hours, 4 hours, and a random value within the range consisting of any two numerical values. If the cationic polymerization time is too short, resulting in a decreased molecular weight; if the cationic polymerization time is too long, it may cause structural instability.

[00120] In the present disclosure, a terminator may be added to discharge and obtain the halogenated branched butyl rubber. The terminator of the present disclosure may be at least one selected from methanol, ethanol, and butanol.

[00121] According to a particularly preferred embodiment of the present disclosure, a mixed solvent ($V_{(diluent)}$: $V_{(solvent)}$ is (70 to 30)/(30 to 70)) and the aforementioned multi-component copolymer are added into a polymerizing pot under an inert atmosphere, stirred and dissolved for 60-70min until the multi-component copolymer is completely dissolved; then cooled to the temperature range from -85°C to -75°C, a diluent, an

isobutene and an isoprene are sequentially added, stirred and mixed until the polymerization system temperature is reduced to the range from -90°C to -85°C, the diluent and the co-initiator are then subjecting to blending and aging at the temperature condition from -100°C to -90°C for 50-60min, the mixture of the diluent and the co-initiator is added into the polymerization system, subjected to stirring and reaction for 3-4h, a terminator is finally added, the reactant is discharged and subjected to coagulating, washing and drying to obtain a halogenated branched butyl rubber;

[00122] wherein the mass ratio of isobutene, isoprene and the multi-component copolymer is 100 : (4-6) : (7-10);

[00123] the mass ratio of the isobutene to the diluent is 100 : (180-320);

[00124] the mass ratio of the isobutene to the co-initiator is 100 : (0.1-0.3).

[00125] The seventh aspect of the present disclosure provides a halogenated branched butyl rubber produced with the aforementioned method.

[00126] The eighth aspect of the present disclosure provides a use of the aforementioned halogenated branched rubber in instrument shock absorbers and electric appliance vibration absorbers.

[00127] The halogenated branched butyl rubber of the present disclosure not only solves the problem that the damping performance is

degraded due to the widening of the effective damping temperature range of the halogenated branched butyl rubber, but also improves the tensile strength and the gas tightness of the halogenated branched butyl rubber, thus the halogenated branched butyl rubber can completely meet the requirements on broad temperature range and damping performance of the electromechanical devices (e.g., an instrument shock absorber and an electrical appliance vibration absorber).

[00128] The present disclosure will be described in detail below with reference to examples.

[00129] If the specific conditions are not indicated in the following examples and comparative examples, the reactions are performed according to the conventional conditions or the conditions suggested by the manufacturers. If the manufacturers of the reagent or instrument are not specified, both the reagent and the instrument pertain to the commercially available conventional products. The mass ratio of structural units contained in the prepared multi-component copolymer product and the halogenated branched butyl rubber are determined according to the feeding amount of raw materials.

[00130] (1) The raw material sources were as follows:

[00131] Isobutylene and isoprene: polymer grade, purchased from Zhejiang Xinhui New materials Co., Ltd.

[00132] P-methyl styrene: polymer grade, purchased from Jiande

Langfeng Chemical Co., Ltd.

[00133] P-butyl styrene: polymer grade, purchased from Luoyang Boyu Energy Technology Co., Ltd.

[00134] P-bromomethyl styrene: polymer grade, purchased from Hubei Shuangyan Chemical Co., Ltd.

[00135] Methyl methacrylate (MMA): commercially available from Tianjin Chemical Reagent No. 2 Plant;

[00136] N-butyl lithium: with a purity of 98%, commercially available from Nanjing Tonglian Chemical Co., Ltd.

[00137] Ethyl aluminum sesquichloride: with a purity of 98%, commercially available from J&K Scientific LLC.

[00138] Other reagents were all commercially available industrial products.

[00139] (2) The analytic testing method:

[00140] The determination of number average molecular weight (Mn) and molecular weight distribution index (Mw/Mn): the two parameters were measured with the 2414 Gel Permeation Chromatography (GPC) manufactured by Waters Corporation in the United States of America (USA). The polystyrene standard sample was taken as a calibration curve, tetrahydrofuran was used as a mobile phase, the column temperature was 40°C, the sample concentration was 1mg/mL, the sample volume was 50 μL, the elution time was 40min, and the flow rate was 1 $mL \cdot min^{-1}$.

[00141] Measurement of the bromine content: 10mg of a sample was weighed, the sample was subjected to a thermal degradation by using a Q600 type TG/DTG thermogravimetric analyzer in a nitrogen atmosphere with a flow rate of 50 mL/min, the temperature rise rate was 10°C/min. The first stage thermal degradation was debromination on a bromine-containing unit of the sample to form HBr, and the bromine content (X) in the sample was reversely deduced from the percentage content of the debrominated HBr, the calculation formula was as follows:

[00142]
$$X = \frac{(100\% - Y) \times 79.904}{79.904 + 1.008}$$

[00143] In the formula: Y denoted the percentage content of said sample at 220°C; 79.904 was the relative atomic mass of bromine element; 1.008 was the relative atomic mass of hydrogen element.

[00144] Measurement of apparent viscosity: the measurement was performed by using the Ubbelohde viscometer according to the China National Standard GB/T 10247-2008.

[00145] Measurement of gas tightness: the air permeability was determined by using an automatic air tightness tester according to the Standard ISO 2782:1995. The test gas was N_2, the test temperature was 23°C, and the test sample was a circular thin sheet with a diameter of 8cm and a thickness of 1mm.

[00146] Dynamic Mechanical Analysis (DMA): the measurement was carried out in tensile mode on the 242C type dynamic mechanical analyzer

manufactured by Netzsch Gmbh, Germany. The sample dimensions were composed of a length of 10mm, a width of 6mm, and a thickness of 2mm, the temperature range was from -90°C to +90°C, the temperature rise rate was 3°C/min, and the data under the frequency of 10 Hz was selected for analysis.

[00147] Tensile strength: the measurement was performing according to the method in the China National Standard GB/T528-2009.

[00148] Example 1

[00149] The example served to illustrate the preparation of a multi-component copolymer.

[00150] Firstly, argon gas was introduced into a 15L stainless steel reaction kettle (i.e., polymerizing pot) with a jacket for replacing air 3 times; 3,000g of hexane, 1,000g of p-bromomethyl styrene, and 5.0g of tetrahydrofuran (THF) were sequentially added into the polymerizing pot, heated to 50°C, 18.5mmo1 n-butyl lithium was added to initiate the reaction performed for 100 min; 300g of p-methyl styrene and 3.0g of THF were then added into the polymerizing pot, further heated to 70°C and carried out the reaction for 60 min; 150g of MMA and 2.0g of THF were subsequently added into the polymerizing pot, the reaction was performed for 40 min; 20g of isoprene was finally added into the polymerizing pot, an end-capping reaction was performed for 20min until the free monomer did not exist, the glue solution was subjected to the wet coagulation and

drying process, the multi-component copolymer S-1 was prepared, wherein the mass ratio of p-bromomethyl styrene, p-methyl styrene, MMA, and isoprene was 100:30:15: 2.

[00151] The measurement results indicated that the multi-component copolymer S-1 had a number average molecular weight (Mn) of 40,100 g/mol, a molecular weight distribution index (Mw/Mn) of 1.45, a bromine content of 4.05%, and an apparent viscosity of 8cps at 25°C.

[00152] Example 2

[00153] The example served to illustrate the preparation of a multi-component copolymer.

[00154] Firstly, argon gas was introduced into a 15L stainless steel reaction kettle (i.e., polymerizing pot) with a jacket for replacing air 3 times; 3,100g of hexane, 1,000g of p-bromomethyl styrene, and 5.4g of THF were sequentially added into the polymerizing pot, heated to 52°C, 19.3mmo1 n-butyl lithium was added to initiate the reaction performed for 105 min; 310g of p-methyl styrene and 3.5g of THF were then added into the polymerizing pot, further heated to 72°C and carried out the reaction for 62 min; 160g of MMA and 2.2g of THF were subsequently added into the polymerizing pot, the reaction was performed for 42 min; 22g of isoprene was finally added into the polymerizing pot, an end-capping reaction was performed for 21min until the free monomer did not exist, the glue solution was subjected to the wet coagulation and drying process, the multi-

component copolymer S-2 was prepared, wherein the mass ratio of p-bromomethyl styrene, p-methyl styrene, MMA, and isoprene was 100:31:16: 2.2.

[00155] The measurement results indicated that the multi-component copolymer S-2 had a number average molecular weight of 42,300g/mol, a molecular weight distribution index of 1.51, a bromine content of 4.21%, and an apparent viscosity of 11.2cps at 25°C.

[00156] Example 3

[00157] The example served to illustrate the preparation of a multi-component copolymer.

[00158] Firstly, argon gas was introduced into a 15L stainless steel reaction kettle (i.e., polymerizing pot) with a jacket for replacing air 4 times; 3,300g of hexane, 1,000g of p-bromomethyl styrene, and 5.7g of THF were sequentially added into the polymerizing pot, heated to 55°C, 21.5mmo1 n-butyl lithium was added to initiate the reaction performed for 110 min; 330g of p-methyl styrene and 4.0g of THF were then added into the polymerizing pot, further heated to 74°C and carried out the reaction for 64 min; 170g of MMA and 2.4g of THF were subsequently added into the polymerizing pot, the reaction was performed for 44 min; 24g of isoprene was finally added into the polymerizing pot, an end-capping reaction was performed for 23min until the free monomer did not exist, the glue solution was subjected to the wet coagulation and drying process, the multi-

component copolymer S-3 was prepared, wherein the mass ratio of p-bromomethyl styrene, p-methyl styrene, MMA, and isoprene was 100:33:17: 2.4.

[00159] The measurement results indicated that the multi-component copolymer S-3 had a number average molecular weight of 45,100 g/mol, a molecular weight distribution index of 1.63, a bromine content of 4.48%, and an apparent viscosity of 14.5cps at 25°C.

[00160] Example 4

[00161] The example served to illustrate the preparation of a multi-component copolymer.

[00162] Firstly, argon gas was introduced into a 15L stainless steel reaction kettle (i.e., polymerizing pot) with a jacket for replacing air 4 times; 3,500g of hexane, 1,000g of p-bromomethyl styrene, and 6.0g of THF were sequentially added into the polymerizing pot, heated to 57°C, 22.6mmo1 n-butyl lithium was added to initiate the reaction performed for 113 min; 360g of p-methyl styrene and 4.4g of THF were then added into the polymerizing pot, further heated to 76°C and carried out the reaction for 66 min; 180g of MMA and 2.6g of THF were subsequently added into the polymerizing pot, the reaction was performed for 46 min; 25g of isoprene was finally added into the polymerizing pot, an end-capping reaction was performed for 25min until the free monomer did not exist, the glue solution was subjected to the wet coagulation and drying process, the multi-

component copolymer S-4 was prepared, wherein the mass ratio of p-bromomethyl styrene, p-methyl styrene, MMA, and isoprene was 100:36:18: 2.5.

[00163] The measurement results indicated that the multi-component copolymer S-4 had a number average molecular weight of 46,500g/mol, a molecular weight distribution index of 1.76, a bromine content of 4.62%, and an apparent viscosity of 20.5cps at 25°C.

[00164] Example 5

[00165] The example served to illustrate the preparation of a multi-component copolymer.

[00166] Firstly, argon gas was introduced into a 15L stainless steel reaction kettle (i.e., polymerizing pot) with a jacket for replacing air 5 times; 3,700g of hexane, 1,000g of p-bromomethyl styrene, and 6.5g of THF were sequentially added into the polymerizing pot, heated to 59°C, 23.4mmo1 n-butyl lithium was added to initiate the reaction performed for 115 min; 380g of p-methyl styrene and 4.8g of THF were then added into the polymerizing pot, further heated to 78°C and carried out the reaction for 68 min; 190g of MMA and 2.8g of THF were subsequently added into the polymerizing pot, the reaction was performed for 48 min; 27g of isoprene was finally added into the polymerizing pot, an end-capping reaction was performed for 27min until the free monomer did not exist, the glue solution was subjected to the wet coagulation and drying process, the multi-

component copolymer S-5 was prepared, wherein the mass ratio of p-bromomethyl styrene, p-methyl styrene, MMA, and isoprene was 100:38:19: 2.7.

[00167] The measurement results indicated that the multi-component copolymer S-5 had a number average molecular weight of 48,900g/mol, a molecular weight distribution index of 1.87, a bromine content of 4.85%, and an apparent viscosity of 24.1cps at 25°C.

[00168] Example 6

[00169] The example served to illustrate the preparation of a multi-component copolymer.

[00170] Firstly, argon gas was introduced into a 15L stainless steel reaction kettle (i.e., polymerizing pot) with a jacket for replacing air 5 times; 4,000g of hexane, 1,000g of p-bromomethyl styrene, and 7.0g of THF were sequentially added into the polymerizing pot, heated to 60°C, 24.8mmo1 n-butyl lithium was added to initiate the reaction performed for 120 min; 400g of p-n-butyl styrene and 5.0g of THF were then added into the polymerizing pot, further heated to 80°C and carried out the reaction for 70 min; 200g of MMA and 3.0g of THF were subsequently added into the polymerizing pot, the reaction was performed for 50 min; 30g of isoprene was finally added into the polymerizing pot, an end-capping reaction was performed for 30min until the free monomer did not exist, the glue solution was subjected to the wet coagulation and drying process, the multi-

component copolymer S-6 was prepared, wherein the mass ratio of p-bromomethyl styrene, p-n-butyl styrene, MMA, and isoprene was 100:40:20: 30.

[00171] The measurement results indicated that the multi-component copolymer S-6 had a number average molecular weight of 49,700g/mol, a molecular weight distribution index of 1.95, a bromine content of 4.98%, and an apparent viscosity of 29.1cps at 25°C.

[00172] Example 7

[00173] The example served to illustrate the preparation of a multi-component copolymer.

[00174] Firstly, argon gas was introduced into a 15L stainless steel reaction kettle (i.e., polymerizing pot) with a jacket for replacing air 5 times; 4,000g of hexane, 1,000g of p-bromomethyl styrene, and 7.0g of THF were sequentially added into the polymerizing pot, heated to 40°C, 16mmo1 n-butyl lithium was added to initiate the reaction performed for 80 min; 200g of p-n-butyl styrene and 5.0g of THF were then added into the polymerizing pot, further heated to 60°C and carried out the reaction for 50 min; 100g of MMA and 3.0g of THF were subsequently added into the polymerizing pot, the reaction was performed for 30 min; 10g of isoprene was finally added into the polymerizing pot, an end-capping reaction was performed for 10min until the free monomer did not exist, the glue solution was subjected to the wet coagulation and drying process, the multi-

component copolymer S-7 was prepared, wherein the mass ratio of p-bromomethyl styrene, p-n-butyl styrene, MMA, and isoprene was 100:20:20: 1.

[00175] The measurement results indicated that the multi-component copolymer S-7 had a number average molecular weight of 25,000g/mol, a molecular weight distribution index of 1.2, a bromine content of 2.5%, and an apparent viscosity of 35.4cps at 25°C.

[00176] Example 8

[00177] The example served to illustrate the preparation of a multi-component copolymer.

[00178] Firstly, argon gas was introduced into a 15L stainless steel reaction kettle (i.e., polymerizing pot) with a jacket for replacing air 5 times; 4,000g of hexane, 1,000g of p-bromomethyl styrene, and 7.0g of THF were sequentially added into the polymerizing pot, heated to 80°C, 30mmo1 n-butyl lithium was added to initiate the reaction performed for 150 min; 500g of p-n-butyl styrene and 5.0g of THF were then added into the polymerizing pot, further heated to 90°C and carried out the reaction for 80 min; 250g of MMA and 3.0g of THF were subsequently added into the polymerizing pot, the reaction was performed for 60 min; 50g of isoprene was finally added into the polymerizing pot, an end-capping reaction was performed for 45min until the free monomer did not exist, the glue solution was subjected to the wet coagulation and drying process, the multi-

component copolymer S-8 was prepared, wherein the mass ratio of p-bromomethyl styrene, p-n-butyl styrene, MMA, and isoprene was 100:50:25: 5.

[00179] The measurement results indicated that the multi-component copolymer S-8 had a number average molecular weight of 60,000g/mol, a molecular weight distribution index of 2, a bromine content of 5.5%, and an apparent viscosity of 40.0cps at 25°C.

[00180] Example 9

[00181] The example served to illustrate the preparation of a multi-component copolymer.

[00182] The multi-component copolymer was prepared according to the method of Example 1, except that 5g of isoprene was added during the preparation process, the multi-component copolymer S-9 was prepared, wherein the mass ratio of p-bromomethyl styrene, p-methyl styrene, MMA, and isoprene was 100:30:15: 0.5.

[00183] The measurement results indicated that the multi-component copolymer S-9 had a number average molecular weight of 39,900g/mol, a molecular weight distribution index of 1.43, a bromine content of 4.09%, and an apparent viscosity of 8.5cps at 25°C.

[00184] Example 10

[00185] The example served to illustrate the preparation of a multi-component copolymer.

[00186] The multi-component copolymer was prepared according to the method of Example 1, except that 60g of isoprene was added during the preparation process, the multi-component copolymer S-10 was prepared, wherein the mass ratio of p-bromomethyl styrene, p-methyl styrene, MMA, and isoprene was 100:30:15: 6.

[00187] The measurement results indicated that the multi-component copolymer S-10 had a number average molecular weight of 41,000g/mol, a molecular weight distribution index of 1.51, a bromine content of 4.01%, and an apparent viscosity of 8.9cps at 25°C.

[00188] Example 11

[00189] The example served to illustrate the preparation of a halogenated branched butyl rubber.

[00190] Firstly, nitrogen gas was introduced into a 4L stainless steel reaction kettle (i.e., polymerizing pot) with a jacket for replacing air 3 times; 350g of dichloromethane, 150g of hexane, and 135g of the multi-component copolymer S-1 were added into the polymerizing pot, stirred and dissolved for 60min until the materials were completely dissolved; then cooled to -75°C; 500g of methane chloride, 500g of isobutene, and 20g of isoprene were sequentially added, stirred and mixed until the temperature of a polymerization system was reduced to -85°C; 50g of methane chloride, 1.05g of ethyl aluminum sesquichloride, and 0.012g of HCl were subjected to mixing and aging under the temperature condition

of -90°C for 50 min, and subsequently added into the polymerization system for stirring and performing the reaction for 3.0h; 15g of methanol was finally added, the reactant was discharged, and subjected to condensing, washing, and drying, a brominated branched butyl rubber product was prepared, wherein the mass ratio of isobutene, isoprene, and multi-component copolymer S-1 in the raw materials for preparation was 100:4:7.

[00191] Sampling and analyzing: the brominated branched butyl rubber was prepared into the standard samples, the test properties were shown in Table 1.

[00192] Example 12

[00193] The example served to illustrate the preparation of a halogenated branched butyl rubber.

[00194] Firstly, nitrogen gas was introduced into a 4L stainless steel reaction kettle (i.e., polymerizing pot) with a jacket for replacing air 3 times; 300g of dichloromethane, 200g of hexane, and 37g of the multi-component copolymer S-2 were added into the polymerizing pot, stirred and dissolved for 62min until the materials were completely dissolved; then cooled to -77°C; 600g of methane chloride, 500g of isobutene, and 22g of isoprene were sequentially added, stirred and mixed until the temperature of a polymerization system was reduced to -86°C; 60g of methane chloride, 1.13g of ethyl aluminum sesquichloride, and 0.015g of HCl were subjected

to mixing and aging under the temperature condition of -92°C for 52 min, and subsequently added into the polymerization system for stirring and performing the reaction for 3.2h; 17g of methanol was finally added, the reactant was discharged, and subjected to condensing, washing, and drying, a brominated branched butyl rubber product was prepared, wherein the mass ratio of isobutene, isoprene, and multi-component copolymer S-2 in the raw materials for preparation was 100:4.4:7.4.

[00195] Sampling and analyzing: the brominated branched butyl rubber was prepared into the standard samples, the test properties were shown in Table 1.

[00196] Example 13

[00197] The example served to illustrate the preparation of a halogenated branched butyl rubber.

[00198] Firstly, nitrogen gas was introduced into a 4L stainless steel reaction kettle (i.e., polymerizing pot) with a jacket for replacing air 4 times; 200g of dichloromethane, 300g of hexane, and 40g of the multi-component copolymer S-3 were added into the polymerizing pot, stirred and dissolved for 64min until the materials were completely dissolved; then cooled to -80°C; 700g of methane chloride, 500g of isobutene, and 24g of isoprene were sequentially added, stirred and mixed until the temperature of a polymerization system was reduced to -87°C; 70g of methane chloride, 1.24g of ethyl aluminum sesquichloride, and 0.021g of HCl were subjected

to mixing and aging under the temperature condition of -94°C for 54 min, and subsequently added into the polymerization system for stirring and performing the reaction for 3.4h; 19g of methanol was finally added, the reactant was discharged, and subjected to condensing, washing, and drying, a brominated branched butyl rubber product was prepared, wherein the mass ratio of isobutene, isoprene, and multi-component copolymer S-3 in the raw materials for preparation was 100:4.8:8.

[00199] Sampling and analyzing: the brominated branched butyl rubber was prepared into the standard samples, the test properties were shown in Table 1.

[00200] Example 14

[00201] The example served to illustrate the preparation of a halogenated branched butyl rubber.

[00202] Firstly, nitrogen gas was introduced into a 4L stainless steel reaction kettle (i.e., polymerizing pot) with a jacket for replacing air 4 times; 700g of dichloromethane, 300g of hexane, and 43g of the multi-component copolymer S-4 were added into the polymerizing pot, stirred and dissolved for 65min until the materials were completely dissolved; then cooled to -81°C; 800g of methane chloride, 500g of isobutene, and 26g of isoprene were sequentially added, stirred and mixed until the temperature of a polymerization system was reduced to -88°C; 80g of methane chloride, 1.36g of ethyl aluminum sesquichloride, and 0.035g of HCl were subjected

to mixing and aging under the temperature condition of -96°C for 56 min, and subsequently added into the polymerization system for stirring and performing the reaction for 3.6h; 20g of methanol was finally added, the reactant was discharged, and subjected to condensing, washing, and drying, a brominated branched butyl rubber product was prepared, wherein the mass ratio of isobutene, isoprene, and multi-component copolymer S-4 in the raw materials for preparation was 100:5.5:8.6.

[00203] Sampling and analyzing: the brominated branched butyl rubber was prepared into the standard samples, the test properties were shown in Table 1.

[00204] Example 15

[00205] The example served to illustrate the preparation of a halogenated branched butyl rubber.

[00206] Firstly, nitrogen gas was introduced into a 4L stainless steel reaction kettle (i.e., polymerizing pot) with a jacket for replacing air 5 times; 500g of dichloromethane, 500g of hexane, and 48g of the multi-component copolymer S-5 were added into the polymerizing pot, stirred and dissolved for 67min until the materials were completely dissolved; then cooled to -83°C; 900g of methane chloride, 500g of isobutene, and 28g of isoprene were sequentially added, stirred and mixed until the temperature of a polymerization system was reduced to -89°C; 90g of methane chloride, 1.41g of ethyl aluminum sesquichloride, and 0.042g of HCl were subjected

to mixing and aging under the temperature condition of -98°C for 58 min, and subsequently added into the polymerization system for stirring and performing the reaction for 3.9h; 23g of methanol was finally added, the reactant was discharged, and subjected to condensing, washing, and drying, a brominated branched butyl rubber product was prepared, wherein the mass ratio of isobutene, isoprene, and multi-component copolymer S-5 in the raw materials for preparation was 100:5.6:9.6.

[00207] Sampling and analyzing: the brominated branched butyl rubber was prepared into the standard samples, the test properties were shown in Table 1.

[00208] Example 16

[00209] The example served to illustrate the preparation of a halogenated branched butyl rubber.

[00210] Firstly, nitrogen gas was introduced into a 4L stainless steel reaction kettle (i.e., polymerizing pot) with a jacket for replacing air 5 times; 300g of dichloromethane, 700g of hexane, and 50g of the multi-component copolymer S-6 were added into the polymerizing pot, stirred and dissolved for 70min until the materials were completely dissolved; then cooled to -85°C; 1,000g of methane chloride, 500g of isobutene, and 30g of isoprene were sequentially added, stirred and mixed until the temperature of a polymerization system was reduced to -90°C; 100g of methane chloride, 1.50g of ethyl aluminum sesquichloride, and 0.065g of HCl were subjected

to blending and aging under the temperature condition of -100°C for 60 min, and subsequently added into the polymerization system for stirring and performing the reaction for 4.0h; 25g of methanol was finally added, the reactant was discharged, and subjected to condensing, washing, and drying, a brominated branched butyl rubber product was prepared, wherein the mass ratio of isobutene, isoprene, and multi-component copolymer S-6 in the raw materials for preparation was 100:6:10.

[00211] Sampling and analyzing: the brominated branched butyl rubber was prepared into the standard samples, the test properties were shown in Table 1.

[00212] Example 17

[00213] The halogenated branched butyl rubber was prepared according to the method in Example 11, except that the multi-component copolymer S-1 was replaced with the multi-component copolymer S-7, the brominated branched butyl rubber product was obtained.

[00214] Example 18

[00215] The halogenated branched butyl rubber was prepared according to the method in Example 11, except that the multi-component copolymer S-1 was replaced with the multi-component copolymer S-8, the brominated branched butyl rubber product was obtained.

[00216] Example 19

[00217] The halogenated branched butyl rubber was prepared according

to the method in Example 11, except that the multi-component copolymer S-1 was replaced with the multi-component copolymer S-9, the brominated branched butyl rubber product was obtained.

[00218] Example 20

[00219] The halogenated branched butyl rubber was prepared according to the method in Example 11, except that the multi-component copolymer S-1 was replaced with the multi-component copolymer S-10, the brominated branched butyl rubber product was obtained.

[00220] Comparative Example 1

[00221] The multi-component copolymer was prepared according to the method of Example 1, except that p-bromomethyl styrene was replaced with methylallyl bromide, the multi-component copolymer D-1 was prepared.

[00222] The halogenated branched butyl rubber was prepared according to the method in Example 11, except that the multi-component copolymer S-1 was replaced with the multi-component copolymer D-1, the brominated branched butyl rubber product was obtained.

[00223] Sampling and analyzing: the brominated branched butyl rubber was prepared into the standard samples, the test properties were shown in Table 1.

[00224] Comparative Example 2

[00225] The multi-component copolymer was prepared according to the

method of Example 3, except that p-bromomethyl styrene was not added during the preparation process, the multi-component copolymer D-2 was prepared.

[00226] The halogenated branched butyl rubber was prepared according to the method in Example 13, except that the multi-component copolymer S-3 was replaced with the multi-component copolymer D-2, the brominated branched butyl rubber product was obtained.

[00227] Sampling and analyzing: the brominated branched butyl rubber was prepared into the standard samples, the test properties were shown in Table 1.

[00228] Comparative Example 3

[00229] The multi-component copolymer was prepared according to the method of Example 4, except that MMA was not added during the preparation process, the multi-component copolymer D-3 was prepared.

[00230] The halogenated branched butyl rubber was prepared according to the method in Example 14, except that the multi-component copolymer S-4 was replaced with the multi-component copolymer D-3, the brominated branched butyl rubber product was obtained.

[00231] Sampling and analyzing: the brominated branched butyl rubber was prepared into the standard samples, the test properties were shown in Table 1.

[00232] Table 1

Example No.	Effective damping temperature range ($\tan\delta \geq 0.3$)	Maximum damping factor ($\tan\delta_{max}$)	Air permeability (cm^3)	Tensile strength (MPa)
Example 11	-53℃ to 65℃	1.933	20.003	22.9
Example 12	-54℃ to 67℃	1.951	20.014	23.0
Example 13	-55℃ to 69℃	1.954	20.031	23.2
Example 14	-56℃ to 70℃	1.959	20.044	23.5
Example 15	-56℃ to 72℃	1.971	20.059	23.7
Example 16	-57℃ to 73℃	1.982	20.072	24.0
Example 17	-52℃ to 63℃	1.926	20.082	22.4
Example 18	-52℃ to 64℃	1.931	20.079	22.7
Example 19	-50℃ to 62℃	1.906	20.091	22.0
Example 20	-51℃ to 63℃	1.917	20.097	22.2
Comparative Example 1	-48℃ to 45℃	1.656	21.097	17.5
Comparative Example 2	-46℃ to 42℃	1.041	21.936	16.1
Comparative Example 3	-42℃ to 31℃	1.692	21.225	20.6

[00233] As can be seen from the results of Table 1, the monomers for preparing the multi-component copolymer in Comparative Examples 1-3 are different from those of the present disclosure, thus the multi-component copolymer in Comparative Examples 1-3 has poor performance in terms of effective damping temperature range, damping performance, gas tightness, and mechanical properties. Compared with the brominated branched butyl rubber products prepared in Comparative Examples 1-3, the brominated branched butyl rubber products prepared in Examples 11-20 of the present disclosure have wider effective damping temperature ranges, better damping performance, better air tightness, and better mechanical property.

[00234] FIG. 1 illustrates a dynamic mechanical spectrogram of a

brominated branched butyl rubber product (Curve #1) prepared in Example 11 of the present disclosure and an existing Brominated Isobutylene Isoprene Rubber (BIIR) 2302 (Curve #2).

[00235] As illustrated by FIG. 1, the brominated branched butyl rubber product prepared in Example 11 of the present disclosure has a larger damping factor within a broad effective damping temperature range than the existing Brominated Isobutylene Isoprene Rubber (BIIR) 2302.

[00236] The halogenated branched butyl rubber prepared in the present disclosure is produced by using a multi-component copolymer as the grafting agent through an addition polymerization instead of an ion substitution, it obstructs the conditions of halogen structure isomerization, improves stability of the effective damping temperature range and the stability of damping performance of the halogenated branched butyl rubber, broadens the application scope of the halogenated branched butyl rubber.

[00237] The present disclosure has no emission of Volatile Organic Compound (VOC) and the byproduct HBr during the preparation process of halogenated branched butyl rubber, the method has the characteristics such as environmental protection, a short technological process, a low production cost, and suitability for the industrial production.

[00238] The above content describes in detail the preferred embodiments of the present disclosure, but the present disclosure is not limited thereto. A variety of simple modifications can be made in regard to

the technical solutions of the present disclosure within the scope of the technical concept of the present disclosure, including a combination of individual technical features in any other suitable manner, such simple modifications and combinations thereof shall also be regarded as the content disclosed by the present disclosure, each of them falls into the protection scope of the present disclosure.